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US Department of the Navy
Office of Naval Research
Atlanta Regional Office
100 Alabama Street NW, Suite 4R15
Atlanta, GA 30303-3104

RE: Grant #: FA9550-06-1-0192
PI: Dr. J R Reynolds
Project #00059866

Enclosed please find one original copy of the above-referenced grant. The final Invention Report is signed by the appropriated University official and thus, fully executed. Two copies of final progress report also attached.

Should you have questions or concerns you may contact our office. We appreciate the opportunity to work with your institution.

Sincerely,

A handwritten signature in black ink, appearing to read "Rosita S Chen".

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Encl.
rc/

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Final Performance Report

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FA9550-06-1-0192

Electroactive Reactive Oligomers and Polymers as Device Components

Reporting Period:

February 1, 2006 to November 30, 2008

John R. Reynolds
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(ii). Objectives

The development of conjugated, conducting and electroactive oligomers, polymers and multi-component materials is proposed for application to photovoltaic, organic electronic and other devices of interest to the Air Force. We will design, synthesize, and characterize oligomers and polymers having a large enhancement of a property or a high degree of tunability of the property *via* repeat unit, macromolecular and morphological structures. Proto-type devices will be studied as a means of providing feedback from materials development and for positioning the materials for transition to industrial or Air Force laboratories.

(iii). Status of Effort

Throughout the AFOSR program entitled “Electroactive Reactive Oligomers and Polymers as Device Components” the Reynolds’ research group at the University of Florida has made great strides in developing π -conjugated telechelic oligomers and fully conjugated polymers for a variety of optoelectronic and redox based device applications of interest to the Air Force. The following nine highlights of the program outline important advances that we have made over this last funding period. Full details for these developments are found in the text of this, and previously submitted, technical reports.

- New π -conjugated polymerization methodologies have been developed continuously throughout this AFOSR program. Our recent development of a base-free Suzuki polymerization allowed the first synthesis of ester and alcohol functionalized polyfluorenes which could be used as blue-green emitters in light emitting devices. The ability to prepare these highly functional polymers, not possible with the normal Suzuki polymerization conditions employed in polyfluorene synthesis, allowed us to prepare alcohol and carboxylic acid functionalized polymers which are processable from water and could be adsorbed on TiO₂ for inclusion into Graetzel-type solar cells. Further, a carboxylic acid-halogen conversion method has been developed for the synthesis of new halo-vinylene functionalized monomers for Suzuki polymerization to provide heterocycle based poly(arylene vinylenes) with a high degree of structural purity and reduced defects relative to polymers obtained via typically used methods. These polymers proved to be efficient light absorbing and hole transport materials in organic solar cell applications.
- Throughout this program, new polymers with enhanced electrochromic capabilities, and especially multicolored polymers which switch to highly transmissive states have been developed. A number of these polymer systems have been licensed to Ciba Specialty Chemicals who is producing them for window and display applications and sampling a number of companies as they look to commercialize electrochromism. The ability to prepare saturated green and deeply colored black electrochromic polymers that switch to highly transmissive states, while also being spray processable, has been accomplished in this last funding cycle. Access to these polymers now allows three color displays and the extension of electrochromic polymers into high contrast electronic paper type devices.

- Spray processable poly(3,4-propylenedioxythiophenes) (PProDOTs) that contain reactive ester pendant groups were accessed via oxidative polymerization. Importantly, these highly spray processable polymers could be defunctionalized after film formation to yield insoluble films with a high degree of electrochromic stability.
- We have synthesized a broad family of reactive telechelic conjugated oligomers based on a variety of electron rich (thiophene, 3 alkylthiophene, 3,4-ethylenedioxythiophene, and dialkoxybenzene) and electron poor (benzo thiadiazole, bis-benzothiadiazole, and thiadiazole/quinoxaline) conjugated units. Telechelic oligomers with diacrylate functionality could be solution processed and patterned using UV-initiated photopolymerization for electrochromic devices. Space charge limited studies yielded mobilities as high as $10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Telechelic alcohol functionalized oligomers have been polymerized into the main chain of polycarbonates to yield materials that form free-standing films with a high content of π -conjugated oligomers.
- Our efforts at developing highly efficient bulkheterojunction (BHJ) solar cells ultimately led to P3HT/PCBM PVDs with power conversion efficiencies of greater than 4%. We have utilized single walled-carbon nantobe (SWNT) thin films for replacing both the hole transporting layer (HTL) and ITO in these PVDs which led us to team with Professor Andrew Rinzler and Nanoholdings LLC to form a company, nRadiance LLC, where these electrodes are being further developed for commercialization of SWNT: conjugated polymer devices. The importance of this work lies in the removal of the acidic PEDOT/PSS HTL which is known to degrade the polymers in typical organic PVDs and PLEDs. We have elucidated the importance of triplet states in organic solar cells by synthesizing a series of Pt-acetylide polymers that have extensive absorption through the visible and into the near infrared region utilizing thiophene and EDOT as donors, along with benzothiadiazole as the acceptor in the polymer backbone. The resultant polymers were found to have absorption peaks of 550-630 nm and bandgaps as low as 1.8eV. The iV characteristics of PCBM based cells yield photoconversion efficiencies of up to 1.45% along with a short circuit current density of 7.18 mA/cm^2 .
- Utilizing an especially electron rich dithienylpyrrole donor (supplied by the Marder group at Georgia Tech) in combination with the very electron poor bis-benzothiadiazole as acceptor, we have synthesized the lowest band gap spray processable polymer prepared to date. Characterizing these polymers on either SWNT films, or thin films on gold in reflection mode, have yielded bandgaps of 0.5-0.6eV. A strong donor acceptor character in these polymers allowed them to be used as the active material in ambipolar polymer field effect transistors with mobility values of 1.2×10^{-3} and $5.8 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for p-channel and n-channel operation, respectively.

- Combining the benzothiadiazole electron acceptor with dithienylsilole electron donors which can pack into ordered structures, we have developed especially high mobility polymers with a broad degree of absorption. Field effect mobilities as high as $0.02\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ have been measured on polymers with absorbances that span from 400 to greater than 800 nm.
- The ability to access both n- and p-doped states in the donor-acceptor polymers have allowed us to construct dual polymer electrochromic devices that are strongly active in the infrared. Initially constructed with both polymers in the neutral state, the devices absorb visible light with the low band gap polymer having an absorption onset of 1.4eV. Application of a bias to the device leads to concurrent oxidation and reduction of the films at the two electrodes and introduction of charge carrier states strongly absorbing in the near infrared and into the mid-infrared.
- A display that effectively functions in variable lighting conditions by switching between a full color reflective electrochromic operation and a light emitting operation has been developed. We utilize a combination of both an electrochromic device and a light emitting electrochemical cell which operates as a reflective ECD when one set of electrodes are biased, and as an LEC when another set of electrodes are biased. The dual EC/EL effect is generated from a single active film material.

IV Accomplishments in Electroactive Polymer/Oligomer Materials and Devices

This report serves as a technical update of the research carried out in the Reynolds research group through funding from the AFOSR from date 1 through November 30, 2008. Prior technical reports compiled year by year accomplishments and the following sections detail successes over the last year. Following the technical details is a comprehensive list of personnel supported, publications generated from the grant, and intellectual property that resulted from this research.

IV. A-1. Neutral green-state conjugated polymers

Conjugated electrochromic polymers (ECPs) that combine high optical contrasts and long-term redox stability with ease in bandgap / color engineering via structural control as well as mechanical deformability address the requirements for flexible electronic systems. Their potential for low-cost scalability and high-throughput solution processing is an additional major appeal when compared to their inorganic counterparts in ultimate applications comprising large-area information displays or portable devices made of finely printed pixel arrays. Further, being operational under a wide range of viewing angles and lighting conditions including direct sunlight, low voltage driven polymeric electrochromic devices (ECDs) promise to impact the development of reflective and transmissive color-changing systems spanning ‘smart’ polychromic glassing technologies and e-papers.

Relying on the concept of energy band mixing induced in a molecular system involving alternating electron rich and poor substituents, we have recently extended the ‘donor-acceptor’ (DA) approach to non-emissive organic electrochromic polymers, opening up new perspectives in completing the palette of colors available.

The DA project started last year, involving a novel and efficient route towards synthesizing soluble conjugated polymers green in the neutral state with high transmissivity upon complete oxidation. From the synthesized materials **1a**, **1b**, **2a**, **2b**, **3a** and **3b** illustrated in **Scheme IV.A-1-1**, green polymers **2a** and **3b** (see **Fig. IV.A-1-2.**) were chosen to demonstrate the potential of this novel class of materials in the context of electrochromism with the perspective of constructing display devices.

Scheme IV. A-1-1.

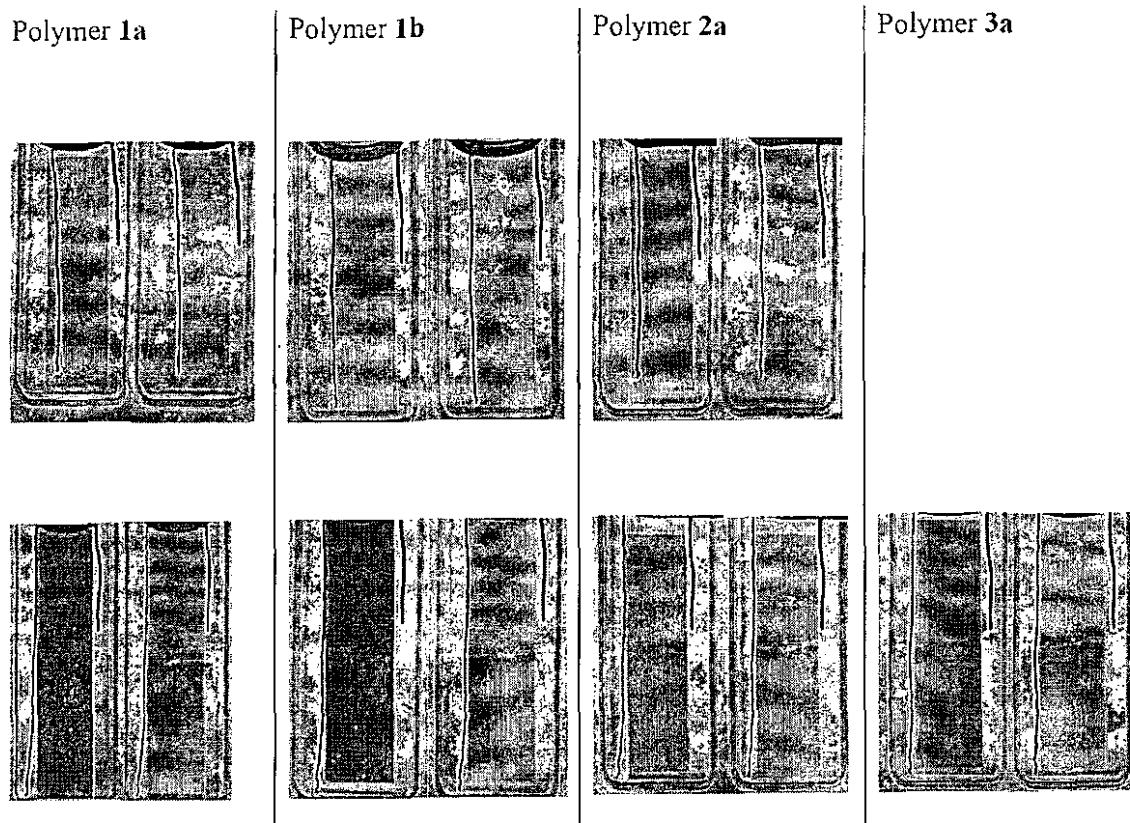
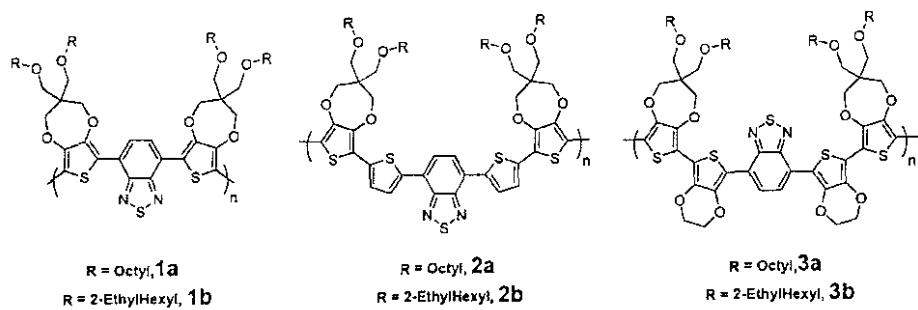


Figure IV. A-1-2. Photographs of the neutral (left) and oxidized (right) polymers **1a**, **1b**, **2a** and **3a** as solid thin or/and thick films spray-cast onto ITO from toluene (**1a**, **1b**, **2a**) or chloroform (**3a**).

While a number of neutral state red and blue ECPs have been synthesized and their properties investigated over the last two decades, attempts in making saturated green polymers, chemically or electrochemically synthesized, have met limited success due to the complex nature of the required absorption spectrum that must contain at least two bands in the neutral state of the material. By understanding the structural parameters that control the absorption spectra of donor-acceptor π -conjugated polymers and applying our reasoning to new synthetic design, we were able to achieve the first processable green-to-transmissive switching polymeric electrochromes following the method described in Fig. IV.A-1-3. a) also detailed in a communication published in *Advanced Materials* (*Adv. Mater.* **20**, 14, 2772 - 277 (2008)).

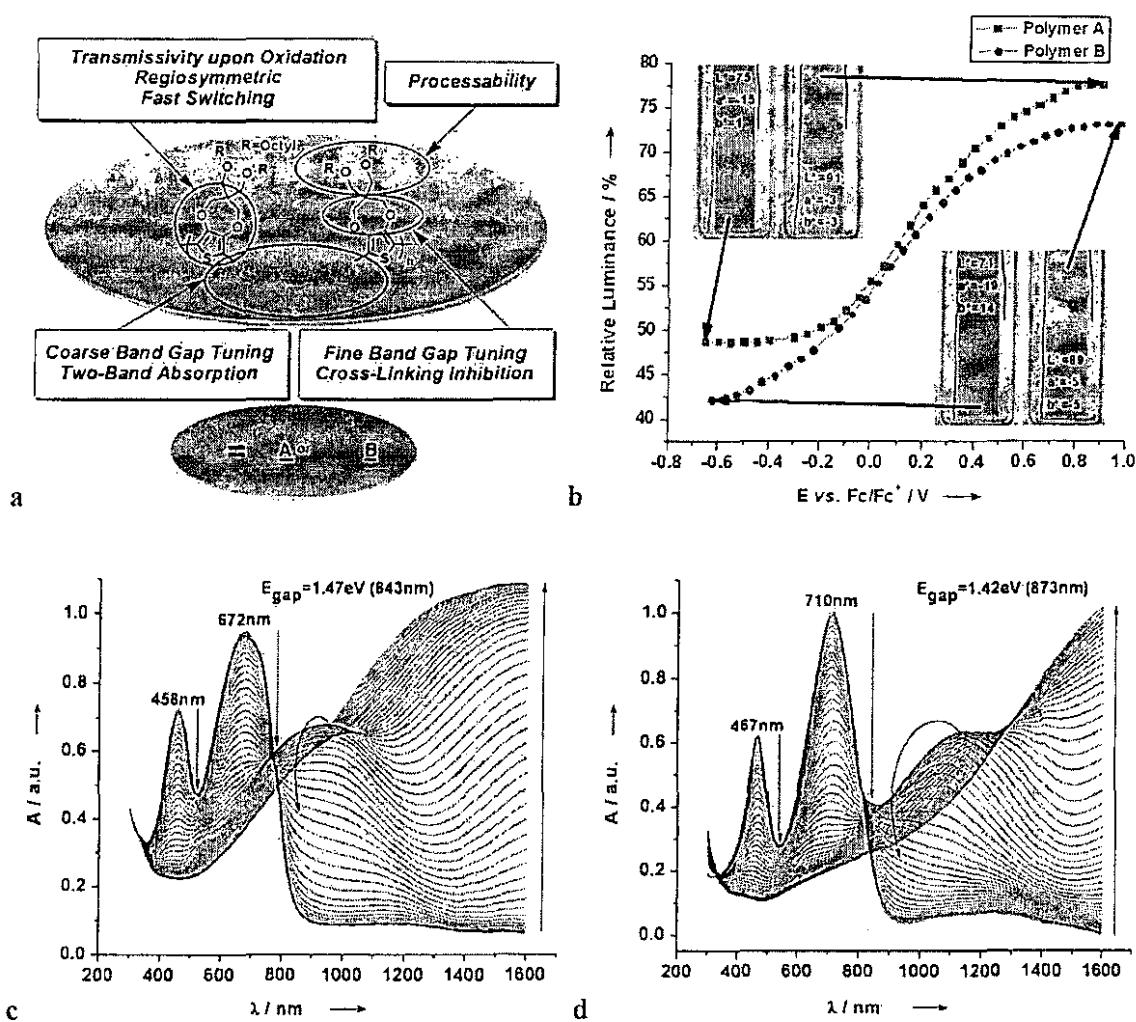


Figure IV. A-1-3. Electrochromic Polymers (ECPs) of Tunable Green. **a**, Two symmetrical donor-acceptor based oligomers were designed, synthesized and chemically polymerized

affording solution-processable conjugated polymers of distinct green hues in their neutral state. The polyheterocyclic hybrids *A* and *B* exhibited highly transmissive oxidized states, excellent optical contrasts both in the visible and in the near infra-red, fast switching times and long-term redox switching stability as expected for practical ECP devices. **b**, Relative Luminance (%) as a function of applied potential for both spray-coated *Polymers A* and *B*. Pictures show the hues of green perceived and give an indication of the degree of transmissivity obtained upon complete oxidation. For color matching, $L^*a^*b^*$ values (in the sense of the CIE 1976 $L^*a^*b^*$ color model) of fully neutral and oxidized states are reported for the films. **c**, Spectroelectrochemistry of *Polymer A* and **d**, *Polymer B* The films were spray-cast onto ITO-coated glass from solution (2 mg mL⁻¹) in toluene (*Polymer A*) or a hot mixture of toluene and chloroform (*Polymer B*). Electrochemical oxidation of the films was carried out in 0.1 M LiBF₄/ACN supporting electrolyte using a silver wire as a quasi-reference electrode (calibrated against Fc/Fc⁺) and a platinum wire as the counter electrode. In both cases, the applied potential was increased in 25 mV steps: -0.4 V ⇌ +0.95 V, *Polymer A*; -0.65 V ⇌ +0.65 V, *Polymer B*.

As illustrated in **Figure IV. A-1-3.**, in our approach for designing conjugated polymers with a two-band absorption in the visible (see **Fig. IV. A-1-3. c** and **d**) so as to reflect and transmit the color green in the neutral state, the acceptor 2,1,3-benzothiadiazole is symmetrically functionalized with different thiophenic donor substituents using repeated palladium mediated cross-coupling reactions. While the first substitution is expected to have the largest impact on the energy gap of the donor-acceptor system, a second substitution with a 3,4-propylenedioxythiophene (ProDOT) (see **Fig. IV. A-1-3. a**) allows fine energy tuning and substantial control over the two-band absorption spectrum of the resulting oligomer. Polymerization of the heterocyclic pentamers gives a distinct optical (red) shift conveniently anticipated by results from various research groups. In addition, as demonstrated earlier in our group, alkoxy-derivatized ProDOT based polymers exhibit sub-second switching times, high EC contrast ratios, redox switching stability, transmissivity of the oxidized state, and a particular ease in synthesis that raises the synthon as a logical building unit in the design of heterocyclic precursors for colored to transparent switching ECPs. Regiosymmetric alkoxy-substituted ProDOTs also possess a low oxidation potential so that mild oxidizing agents can be used for polymerizing the designed oligomers which limits the risks of cross-linking occurring during the polymerization and induces solution-processability to the subsequent polymers. For a polymeric material transmitting / reflecting green light, obtaining a highly transmissive state upon oxidation is an additional major difficulty due to the requirement for simultaneous and efficient bleaching of the two absorption bands that occurs in the blue and red portions of the visible region. Here, the synthesized polymers attain high transmissivity upon complete oxidation (see **Fig. IV. A-1-3. b**, **c** and **d**) along with being solution-processable.

IV. A-2 Neutral black-state conjugated polymers

While exploring the use of the donor-acceptor approach in designing novel DA-ECPs exhibiting a two-band optical absorption in the visible with the goal of achieving saturated

greens, we demonstrated that by varying the relative contribution of electron rich and poor heterocycles incorporated in the repeat unit the low and high energy transitions could be tailored in a substantial and interconnected fashion (see Fig. IV. A-2-1). Through synthetic design, we showed that a balance can be found between short and long wavelength absorption bands in terms of their relative intensities and observed a simultaneous merging of the bands (see Fig. IV. A-2-1 b) and d)) that offers perspectives for the synthesis of neutral state colored materials possessing either highly saturated or darker colors.

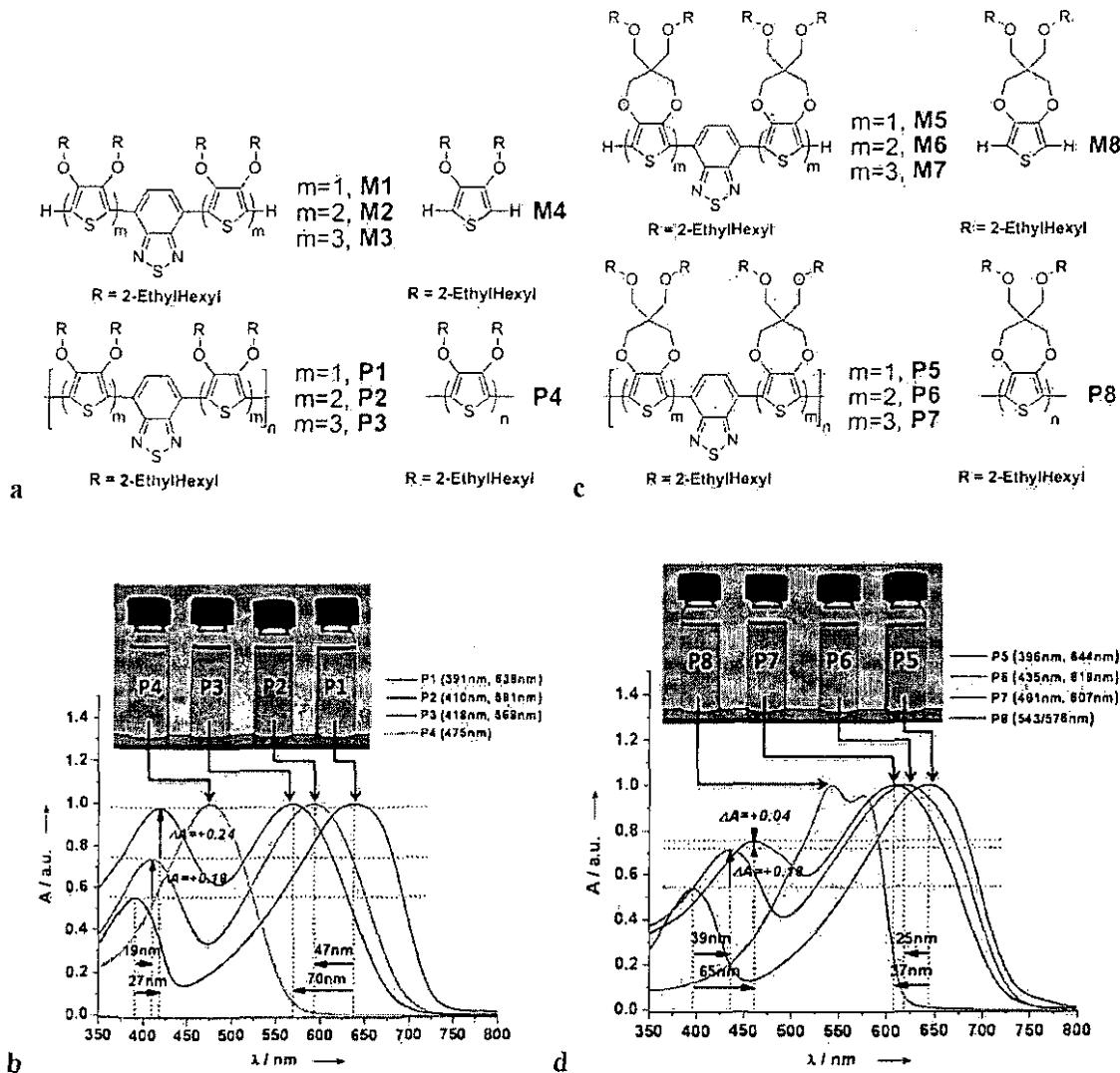


Figure IV. A-2-1. Visible absorption of P1 to P8. a, Molecular structure of M1, M2, M3, M4, P1, P2, P3 and control polymer P4. b, Solution optical absorbance spectra of polymers P1, P2, P3 and control polymer P4 in toluene (spectrum of each system is normalized at the longer wavelength absorption maximum) c, Molecular structure of M5, M6, M7, M8, P5, P6, P7 and

control polymer **P8**. **d**, Solution optical absorbance spectra of polymers **P5**, **P6**, **P7** and control polymer **P8** in toluene (spectrum of each system is normalized at the longer wavelength absorption maximum). Legends specify the values of the respective absorption maxima for both high and low energy transitions. Pictures illustrate the colors obtained upon polymerization of each system.

Based on the empirical observations described above, a soluble copolymer possessing an absorption spectrum extending over the entire visible region (400 - 700nm) was synthesized and its redox properties investigated, demonstrating the first black to transmissive switching polymeric electrochrome (see Figure IV. A-2-2.). This work was described in a letter published in *Nature Materials* (*Nat. Mater.* 7, 795 - 799 (2008)). At a time where ECPs combining mechanical flexibility, color tunability via structural control, high contrast ratios, and fast response times, along with long-term optical stabilities are proving useful in the fast-developing area of color-changing electronics for reflective / transmissive device applications, it is expected that processable black to transmissive analogues will impact the development of EC windows, e-papers and flexible displays in general by providing lower fabrication and processing costs via printing, spraying, and coating methods, along with good scalability when compared to their traditional inorganic counterparts (such as WO_3).

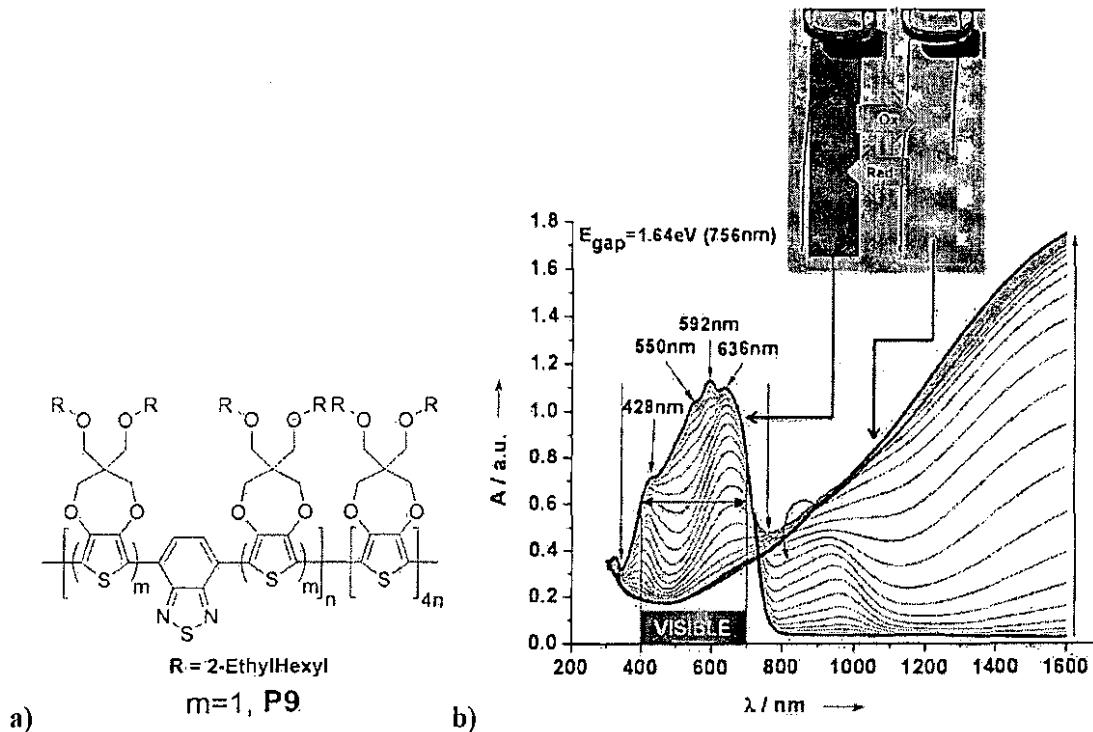


Figure IV. A-2-2. Spectroelectrochemistry of Polymer **P9**. **a**, Molecular structure of copolymer **P9**. **b**, Spectroelectrochemistry of Polymer **P9** with its respective band gap as estimated from the

onset of absorption. The film was spray-cast onto ITO-coated glass from solution (4 mg mL^{-1}) in toluene (Abs. 1.14 a.u.). The applied potential was increased in 25 mV steps: $+0.04 \text{ V} \Leftrightarrow +0.74 \text{ V}$. Pictures illustrate the colors of **P9** obtained upon electrochemical switching both in the neutral state (left) and upon full oxidation (right).

IV. A-3. Reactive oligomers

i. Telechelic conjugated oligomers system based on N-alkyl proDOP

As shown above and earlier AFOSR reports, we are able to make electrochromic devices with a great variety of color contrasts, such as yellow to blue, green and black to transmissive. Meanwhile, we are drawn to build the correlations between materials properties and device performance. From this aspect, oligomers that have discrete chromophores and well-defined structures provide a more ideal platform than polymers do, since polymers usually are a mixture of chromophores with different conjugation lengths.

Solution-processable anodically coloring N-alkyl 3, 4-propylenedioxypyrole (ProDOP) polymers have been found excellent electroactive materials for electrochromic devices. Here, a set of ProDOP-based oligomers with discrete chromophore are presented (**Figure IV-A-3-1**) and their electrochromic studies have been performed in the course of understanding materials properties and device performance.

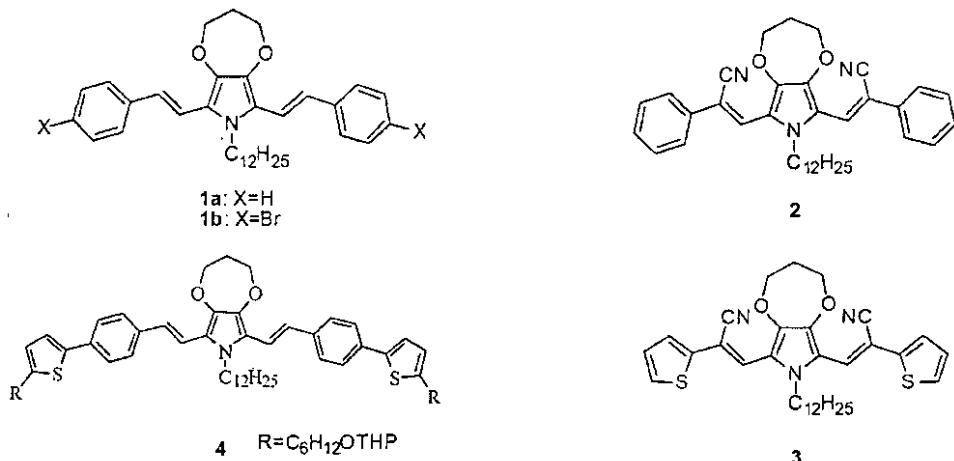


Figure IV-A-3-1: Molecular structures of ProDOT-based oligomers

Spectroelectrochemistry data of the film can not be achieved, due to the high solubility of those oligomers in organic solvent. One way to solve this problem is by studying the solution doping process of the oligomers and observing the color change during the different oxidation states (**Figure IV-A-3-2**).

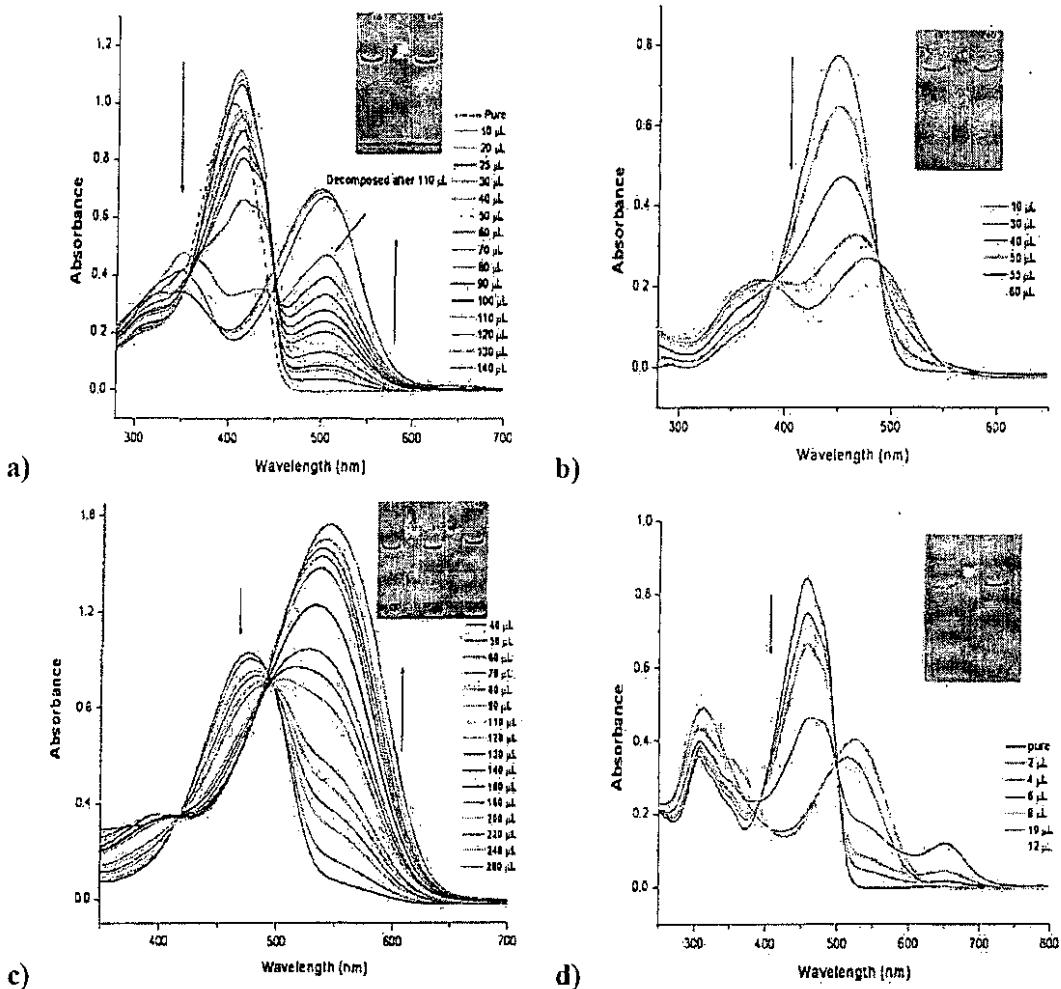


Figure IV-A-3-2. Solution doping of the oligomer compounds **1a**, **2**, **3** and **4** was carried in DCM using nitrosonium hexafluorophosphate (NOPF₆) as the oxidant. a) **1a**, oxidized with a 1 mM NOPF₆/DCM solution from 10-140 μL, b) **2**, oxidized with a 0.5 mM NOPF₆/DCM solution from 10-60 μL, c) **3**, oxidized with a 0.5 mM NOPF₆/DCM solution by adding 5-280 μL, and d) **4**, oxidized with a 0.5 mM NOPF₆/DCM solution by adding 2-12 μL.

Both compounds **1a** and **2** are yellow in their neutral state. Upon oxidation, compound **1a** became a red color while the neutral state peak at around 430 nm decreased and another peak at around 510 nm emerged. The compound can be reversibly oxidized and neutralized below a critical level. Compound **2** became nearly colorless on oxidation, following the disappearance of the absorption peak at around 460 nm, which means the process was not reversible and the compound was decomposed under oxidized state. The neutral solution of compound **3** was a yellow color. After doping solution was added, the intensity of the low wavelength peak

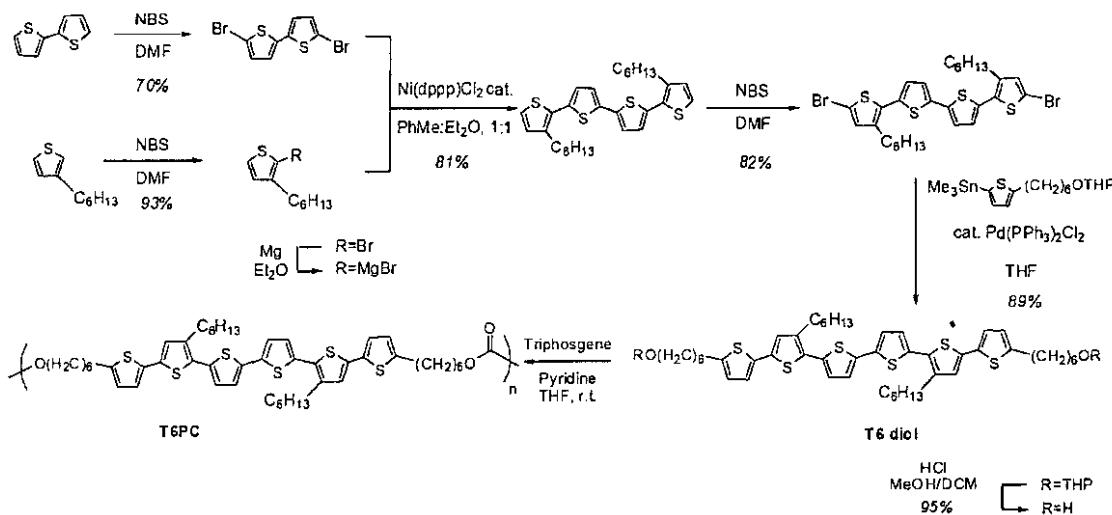
decreased while a lower energy peak centered around 550 nm emerged. The oligomer solution went from a yellow color to a purple color, passing through a light red at intermediate doping levels. The doping process of compound 4 showed a decreased intensity of neutral absorption peak at around 450 nm, two new upcoming peaks at 520 nm and 650 nm, however the whole process was not reversible.

ii. Main-chain Polymers

Low-cost organic thin-film transistors are based on materials which count high mobility, air stability and ease of processing as their main characteristics. Intense research has focused on oligo- and polythiophenes, as such materials early showed high hole mobilities. While vapor deposited α -sexithiophene oligomer thin films transistors have proven to be efficient in devices, their hole mobility decreased significantly when made by solution processing, ordering being an issue here. The solution-processable alternative poly(3-hexylthiophene) has shown great potential but being sensitive to atmospheric oxygen, air stability now becomes an issue. The research conducted in this project focuses on the study of a soluble polymer consisting of discrete sexithiophene oligomers (T6) regularly linked by aliphatic chains, newly synthesized from the corresponding telechelic oligomer, as a potential candidate for OTFT applications. This material already shows good solution processability, and will hopefully exhibit significant hole mobilities after proper thermal treatment.

Telechelic T6 diol was prepared via a sequence of bromination and transition-metal catalyzed couplings. Various conditions were screened for the polymerization of the telechelic diol, among which the use of triphosgene in the presence of pyridine as a base in THF showed best results. Under such conditions, T6PC with number average molecular weights of 20,000 g/mol and higher were synthesized with high purity according to NMR and elemental analysis (**Scheme IV-A-3-1**).

Scheme IV-A-3-1



Differential scanning calorimetry (DSC) and polarized optical microscopy (POM) experiments show that the polymer might exhibit liquid-crystalline phases (Figure IV-A-3-3).

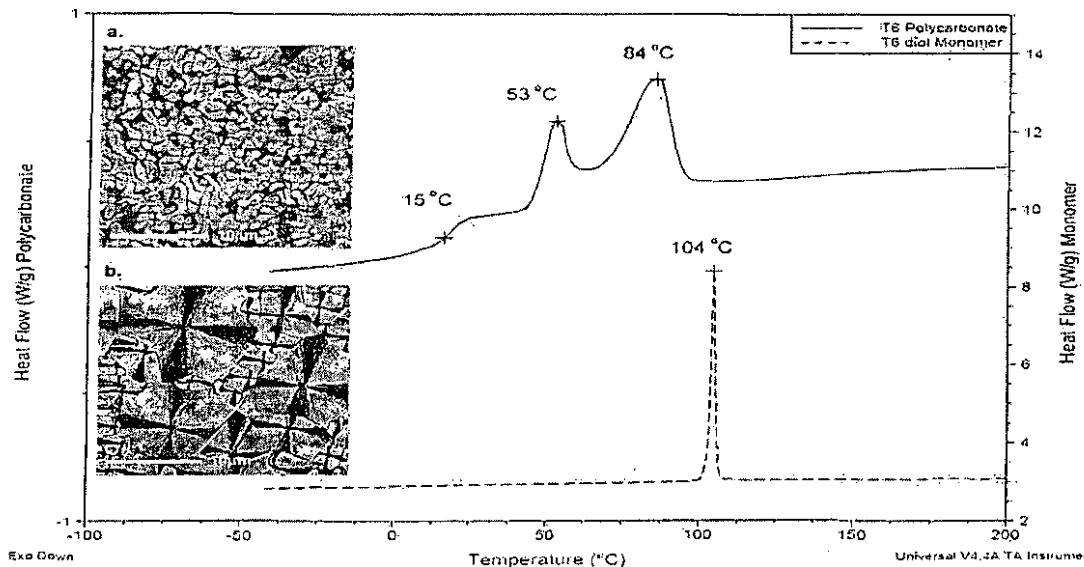


Figure IV-A-3-3: Heating curves for DSC experiments: T6 diol monomer (Right bottom) and T6PC (Right top); Polarized optical microscope images: T6 diol monomer (Left bottom) and T6PC (Left Top)

The polymer T6PC being soluble in a selection of solvents, it can be easily spray-cast from a chloroform solution onto ITO coated glass, which served as the working electrode for cyclic voltammetry (CV). The spectroelectrochemistry experiments carried out on the polymer solid films (Figure IV-A-3-4) show strong color changes as carriers are introduced.

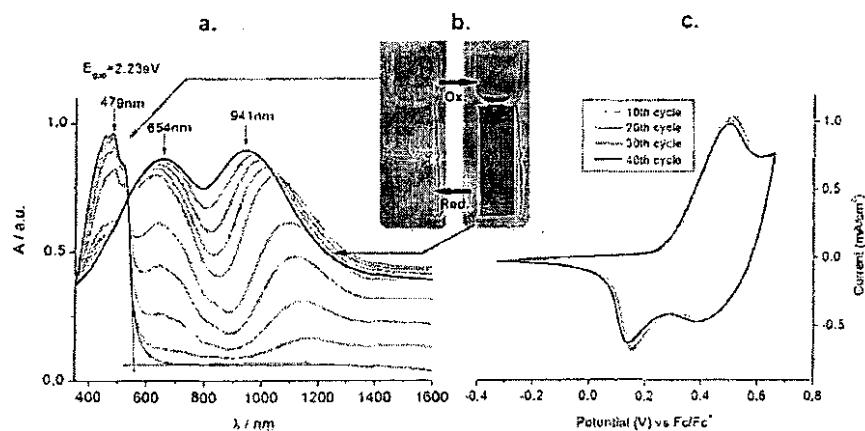


Figure IV-A-3-4 a). Spectroelectrochemistry of the film recorded in a 0.1M solution of LiClO_4 in acetonitrile. The absorption band of the neutral polymer at $\lambda_{\text{max}}=479\text{nm}$ decreases upon

oxidation as two new absorption bands in the blue and near-IR regions appear from the formation of polarons and bipolarons in the oxidized film, b). The films switch from yellow to blue with good stability over 40 cycles, and c) Cyclic voltammograms, up to 40 cycles, recorded in a 0.1M solution of LiClO₄ in acetonitrile versus ferrocene.

IV-A-4. 3, 6-Linked Carbazole Polymers

Polycarbazoles are materials of potential interest in organic electronics due to their photoluminescent and electroluminescent properties and high hole-transport mobility. Carbazole-based polymers were used in OFETs and in OLEDs. Recently, very promising results were demonstrated when using 2,7-linked poly(thiophene-carbazole) derivatives in organic solar cells. However, the photovoltaic properties of 3,6-linked carbazole polymers have not been studied so far. Here, we chose a 3,6-linked poly(thiophene-carbazole) as a model polymer for photovoltaics. The final aim of this project is to covalently graft fullerene derivatives on the polymer to study the effect of a ‘fullerene polymer’ on the morphology and performances of photovoltaic devices. A poly(3,6-bithiophenecarbazole) with an ester-functionalized alkyl chain (3,6-PBTC) was synthesized. The ester group is likely to enable further functionalization of the polymer.

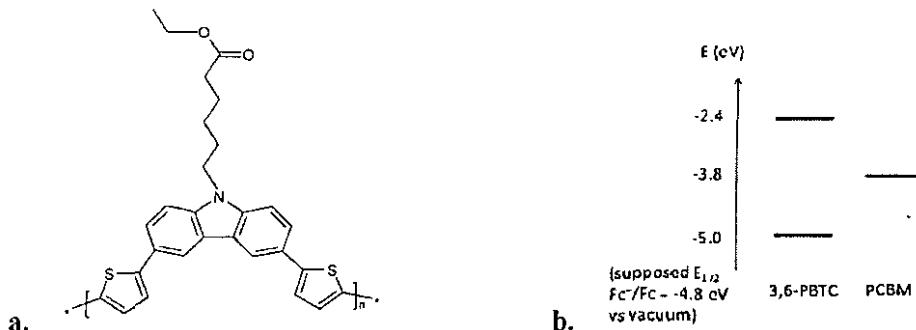


Figure IV-A-4-1 a) Chemical structure of p-3,6-PBTC, and b) HOMO and LUMO energy levels of p-3,6-PBTC.

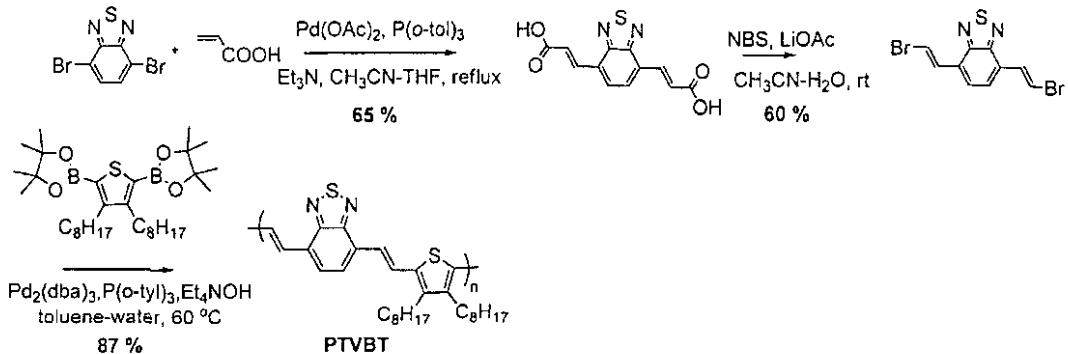
p-3,6-PBTC was synthesized through oxidative polymerization of the 3,6-bithiophenecarbazole monomer in presence of FeCl₃. The polymer structure was confirmed by ¹H NMR. The UV-Vis absorbance spectrum exhibits a maximum at 420 nm and an onset at 500 nm (in solid state), in good agreement with the electrochemical gap of 2.6 eV determined by cyclic voltammetry from the onsets of the oxidation and reduction peaks. The HOMO and LUMO energy levels are estimated to be -5.0 eV and -2.4 eV *vs* vacuum respectively (with E_{1/2} Fe⁺/Fe taken to be -4.8 eV *vs* vacuum). Given the LUMO energy level of PCBM of -3.8 eV *vs* vacuum, charge transfer from the donor polymer to the acceptor is likely to occur. Photovoltaic tests have shown good incident photon to current conversion efficiency in the blue region of the visible spectrum and relatively high open-circuit voltages in bulk heterojunction solar cells with PCBM (*cf.* section IV-B-2-ii below).

IV. A-5. PTVBT synthesis

Low bandgap donor-acceptor alternating conjugated polymers have received considerable interests as active materials for organic photovoltaics (OPVs), light-emitting diodes (OLED) and electrochromic devices. The typical donor-acceptor conjugated polymers are made of electron-deficient nitrogen-containing aromatic heterocycles (2,1,3-benzothiadiazole, [1,2,5]thiadiazolo[3,4-g]quinoxaline, and benzo[1,2-*c*;3,4-*c*]bis[1,2,5]-thiadiazole, etc) as effective acceptors and electron-rich derivatives (thiophene, alkoxoybenzene, carbazole and fluorene , etc.) as donors. Vinylene-linked donor-acceptor (VDA) conjugated polymers are another type in the low bandgap polymer category that has a vinylene linkage between donor and acceptor groups. An advantage of incorporating vinylene linkages is that they serve to planarize the polymer backbones by erasing torsional interactions between donor and acceptor rings and extend conjugation length, which could lead to a decreased bandgap. In addition, introducing flexible vinylene groups into polymer bones could partially increase polymer solubility so that chromophore concentration can be increased by using less solubilizing groups.

The Reynolds group has developed a facile approach to prepare defect-free VDA conjugated polymers. The vinylene-linked benzothiadiazole-thiophene (**PTVBT**) polymer has been chosen to demonstrate the chemistry. The synthesis of **PTVBT** is shown in **Scheme IV-A-5-1**.

Scheme IV-A-5-1



Differential pulse voltammetry (DPV) was employed to estimate the absolute energies of the HOMO and LUMO levels and the magnitude of the band gap (**Figure IV-A-5-1-a**). Polymer appeared to be electrochemically stable in oxidative range of potentials (p-doping between -0.2 and +0.9 V vs Fc/Fc⁺). n-doping process was less stable than p-doping switching: the current of n-type peak at -1.72 V decrease significantly after the second redox scan. Spectroelectrochemical measurement was performed to determine its electrochromic properties. **Figure IV-A-5-1-b** shows the oxidative spectroelectrochemistry for **PTVBT**. In the neutral form of the polymer (+0.2 V vs Fc/Fc⁺) two absorption maxima at 416 and 633 nm are observed, which correspond to the π-π* transitions of the polymer and induce deep blue color to the film. Upon oxidation these

transitions vanish with simultaneous formation of a broad peak outside the visible region at longer wavelength, associated with low energy charge carriers (polarons and bipolarons). When the film is completely oxidized ($+0.85$ V vs Fc/Fc^+), it turns to a pale blue color. Band gap (E_g) has been determined by the onset of the $\pi-\pi^*$ absorption for the neutral form of the polymer and appeared to be relatively low around 1.52 eV.

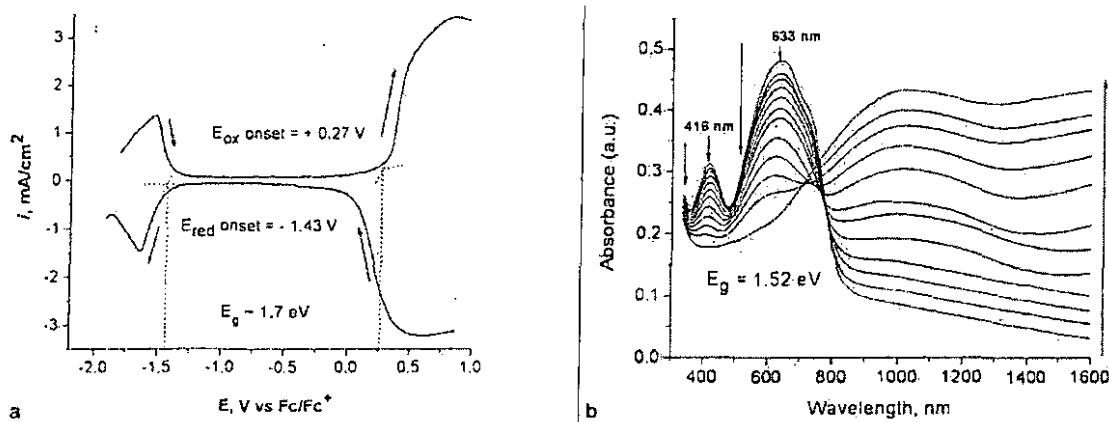
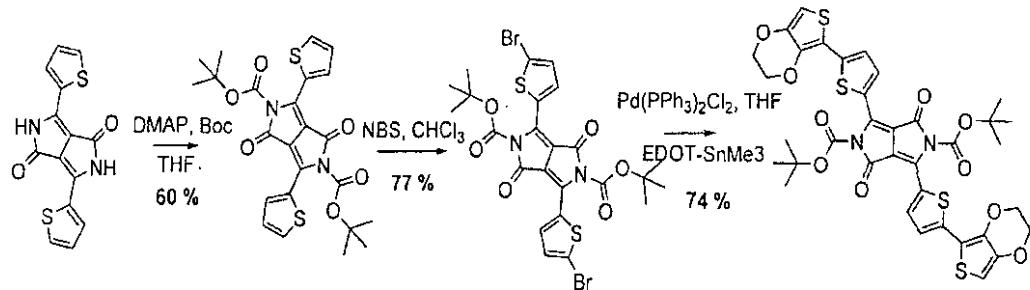


Figure IV-A-5-1 a) Differential pulse voltammetry (DPV) of PTVBT, electrochemical p-doping and n-doping processes of PTVBT on Pt button electrode in 0.1M TBAP/PC in a dry box, and b) Spectroelectrochemistry of PTVBT, spray cast on ITO/glass from 3 mg/mL solution of the polymer in toluene in 0.1M TBAP/PC between 0.2 and 0.85V in 50mV steps (vs Fc/Fc^+).

IV. A-6. DPP oligomer synthesis

3,6-diphenyl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione and its derivatives are famed as brilliant high-performance pigments exhibiting outstanding durability and excellent thermal stability. The desire to build electrochromic devices with high optical contrasts, fast switching speeds, and a long life-time leads us to investigate DPP-based oligomers. The synthesis of the first electropolymerizable DPP oligomer with thermal-cleavage protecting group is outlined in Scheme IV-A-6-1.

Scheme IV-A-6-1



IV Organic Electronic Device Development

IV-B-1. Facilities and technique development

Our research group has continued to develop our device facilities to extend our fabrication and characterization capabilities. Our device laboratories have recently expanded with the addition of a new approximately 750 sq. ft. laboratory, the allocation of which is due, at least in part to the strong research efforts of our group. This new two-room laboratory will be used for device characterization and performance measurements. Also a recent addition to our facilities is a new Veeco Innova scanning probe microscope (Figure IV-B-1-1). This microscope along with additional accessories gives us the capabilities to analyze devices using atomic force microscopy (AFM), scanning tunneling microscopy (STM), conductive AFM, and Electrostatic Force Microscopy. In our fabrication laboratory we have added a vacuum oven inside our glovebox allowing us to dry and vacuum anneal at programmable temperatures. We are also in the process adding a clean bench which will help in producing defect free thin films and devices. An optometer with a calibrated large area silicon photodiode and a calibrated germanium photodiode coupled to an integrating sphere has also been added. This gives us the ability to accurately measure radiant emittance and calculate external quantum efficiencies for OLEDs and PLEDs over the visible and near infrared regions of the electromagnetic spectrum. The addition of these new tools seems to give us a complete arsenal in our quest to expand the frontiers of organic electronic devices. We have fabrication and characterization capabilities inside the inert atmosphere of an argon glovebox for charge transport devices, light emitting diodes, and photovoltaic cells. We also have full optical and morphological characterization capabilities.

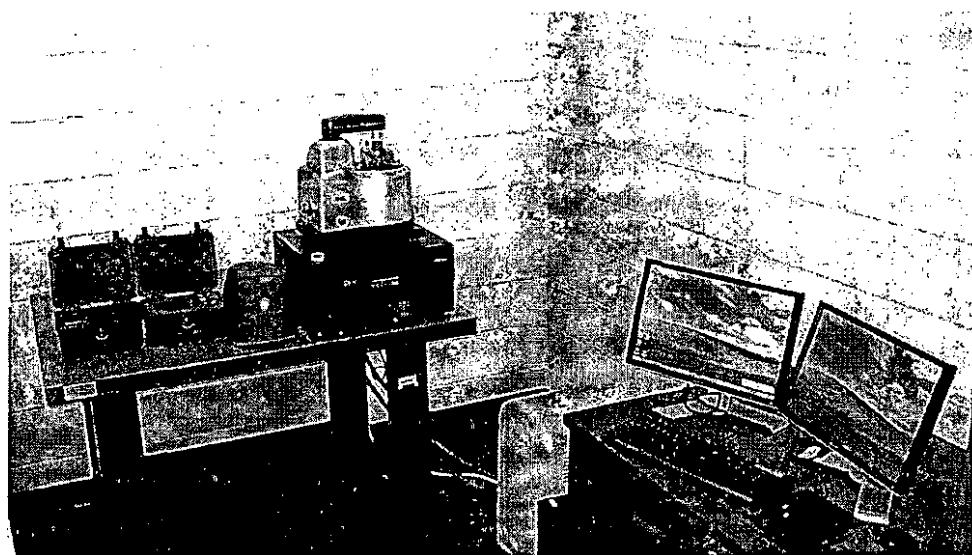


Figure IV-B-1-1 Veeco Innova scanning probe microscope

IV-B-2 Conjugated polymer photovoltaics

i. General devices

This past research year we have continued to pursue narrow bandgap polymers for use in photovoltaics. Though poly(3-hexylthiophene-2,5-diyl) (P3HT) remains at the pinnacle of polymer based solar cell results, the optical band gap of P3HT is approximately 630 nm(1.9 eV) and hence the absorption spectrum drops to zero above this value. This renders all photons of greater wavelengths useless in a P3HT cell. Switching to a material with a bandgap of 850 nm (1.46 eV) would double the number of available incident photons. Of course there are other considerations in perfecting polymer solar cells, but better coverage of the solar spectrum is of obvious importance.

An ideal candidate for polymer photovoltaics should have strong absorption into long wavelengths, but still have a LUMO level 0.3-0.4 eV above the electron acceptor to overcome exciton binding energies. It is also important that the HOMO level of the polymer be deep enough so as to prevent polymer oxidation. Polymer HOMO levels should be at least -5.0 eV to for stability reasons. Also, of important consideration (and possibly the reason for superior performance of P3HT) is high charge mobility.

ii. Carbazole polymers

While synthetic work nears completion for 3-6 linked carbazoles we have demonstrated photovoltaic behavior from 3,6-PBTC and examined morphology trends in polymer/PCBM blend films. Photovoltaic devices were made of the multi-layer construction: Glass/ITO/PEDOT:PSS/3,6-PBTC/PCBM/Aluminum. The blend active layer was varied in thickness and weight/weight ratios. Devices were analyzed for photovoltaic performance by measuring both A. M. 1.5 Power Conversion Efficiency (PCE) and Incident Photon to Current Efficiency (IPCE) measurements. Surface morphology and film thickness measurements were studied using our Innova AFM in tapping mode.

Figure IV-B-2-1 shows the J-V trace of the device producing the highest power conversion efficiency. This cell was made with a polymer: PCBM blend film containing 30% polymer by weight. This device exhibited an open circuit voltage (V_{oc}) of 0.75 V, and a short circuit current (I_{sc}) of 1.67 mA/cm². The fill factor was 0.35 and overall power conversion efficiency was 0.43% (*Fig. 2*). These devices exhibited high open circuit voltages which increased linearly with increasing percentages of polymer in the blends, however, this increase was accompanied by corresponding decreases in short-circuit currents. We hope that improvement to the polymer-fullerene interface will lead to increases in the photocurrent.

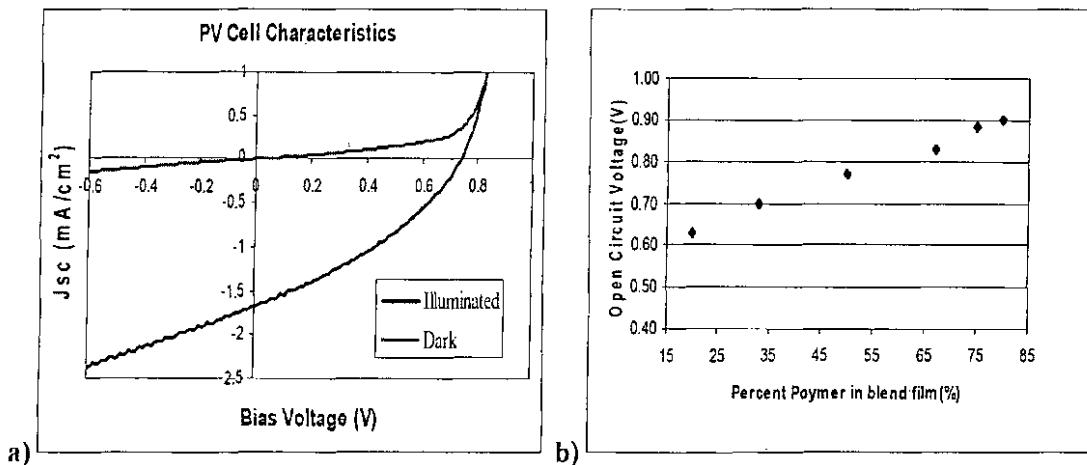


Figure IV-B-2-1. a) J-V trace in the dark and under A.M. 1.5 simulated radiation of intensity $100 \text{ mW}/\text{cm}^2$ of a 3,6-PBTC/PCBM bulk heterojunction solar cell containing 30 wt% polymer spin-coated from chlorobenzene, and b) Increasing open circuit voltage trend with increasing polymer percentages.

The IPCE measurements revealed external quantum efficiencies over 40%. This maximum occurring at 420 nm corresponds to the maximum of absorbance of the 3,6-PBTC (**Figure IV-B-2-2**). A slight red-shift in photoluminescence was observed with increasing PCBM content. Morphology studies of blend films of varied polymer percentages showed a peak in roughness with the peak in device performance as can be seen. Though overall efficiencies are low, the 3,6-PBTC system will likely provide an interesting study of film morphology and interfacial modification through PCBM linkages.

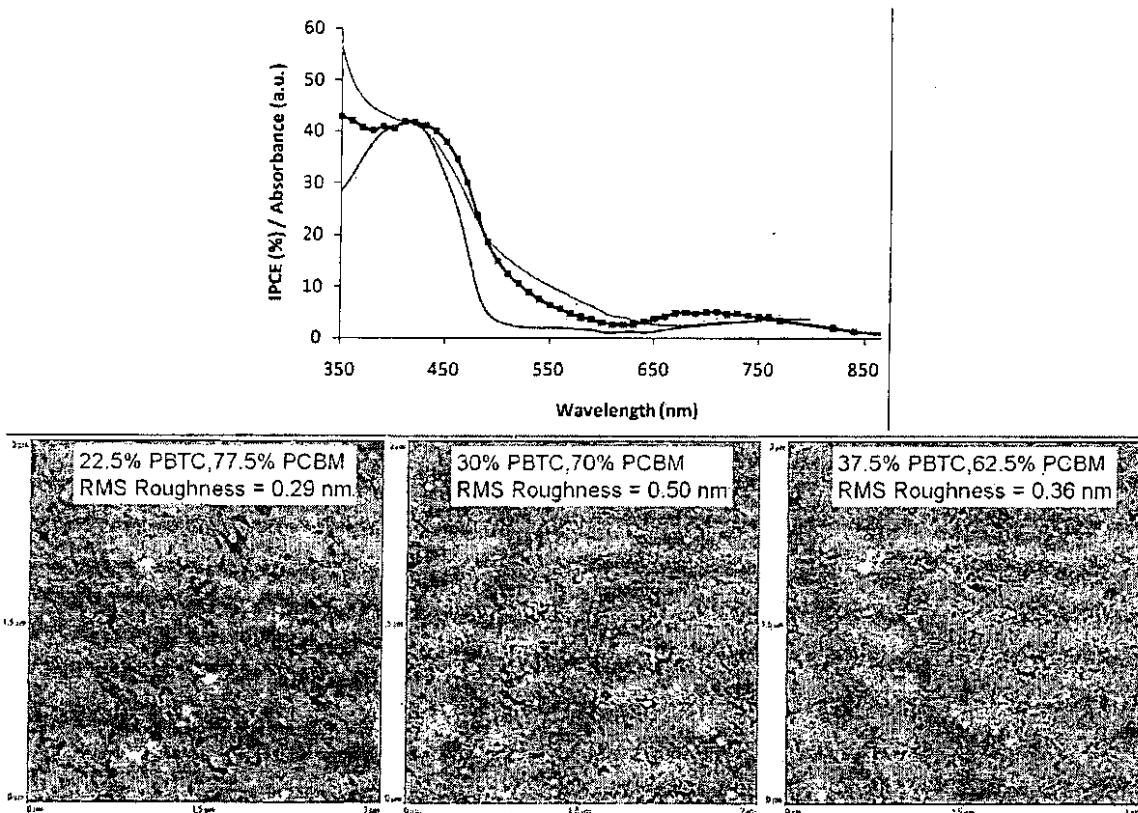


Figure IV-B-2-2. Top: IPCE(dark red) and UV/Vis absorbance (blue) of the same solar cell. UV/Vis absorbance of a 3,6-PBTC film (green). Bottom: 3x3 micron AFM images differences in film morphologies between blend films varying from 22.5 to 37.5 weight percent polymer.

iii. PTVBT polymer

Our research with narrow band gap polymers for photovoltaic applications has involved the newly synthesized PTVBT, with an absorption spectrum extending to above 800 nm (**Figure IV-B-2-3**), making it an attractive candidate for use in photovoltaics. This broad absorption spectrum offers the potential to absorb approximately twice as many photons as P3HT-based active layers. Differential Pulse Voltammetry (DPV) results indicate that the LUMO level of PTVBT is well positioned at -3.7 eV to use PCBM as an electron acceptor. The HOMO level is at approximately -5.3 eV which should provide for good stability. We have fabricated cells with the layered architecture: ITO/PEDOT:PSS/PTVBT:PCBM/Al. Device performance was characterized through measurements of incident photon to current efficiency (IPCE) and A.M. 1.5 power conversion efficiency (PCE). A thorough AFM study investigated the film morphologies and layer thicknesses.

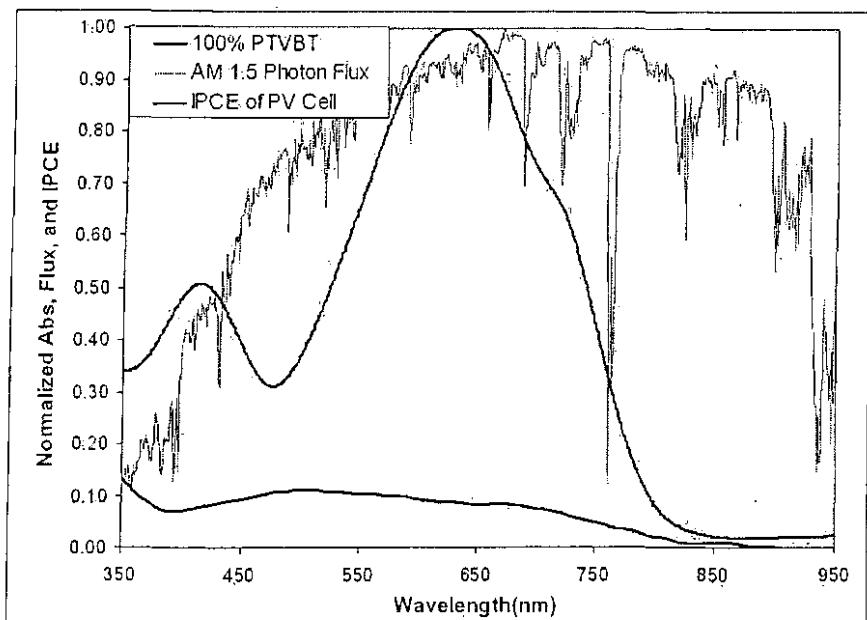
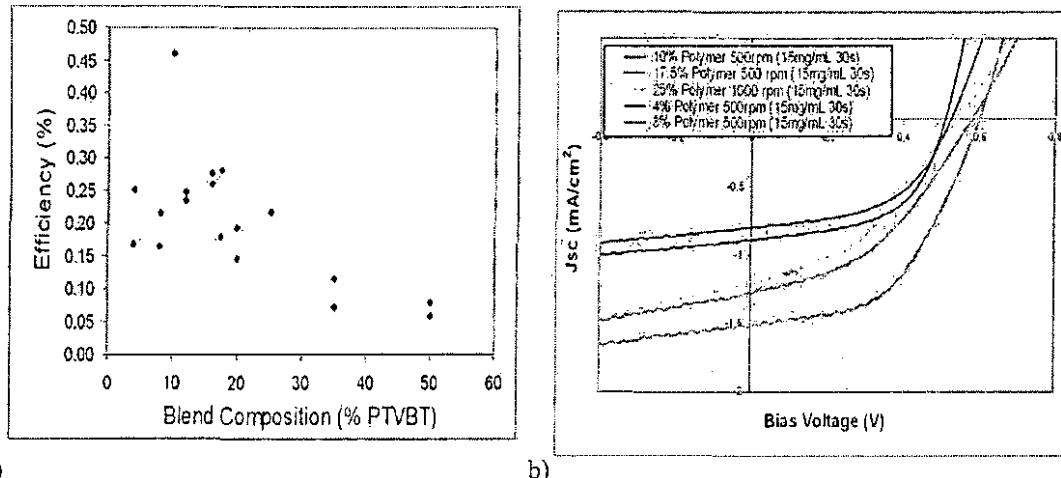


Figure IV-B-2-3. The normalized Photon Flux, and the PTVBT absorption spectrum. IPCE results for a PTVBT cell are displayed for a typical cell.

Though the photovoltaic fabrication has not been fully optimized A.M. 1.5 power conversion efficiencies of 0.46% have been reached. Variation of the blend film weight percentage of PTVBT to PCBM resulted in optimal performance with surprisingly low polymer percentages (approximately 10-15%) which is shown in **Figure IV-B-2-4**. It should be kept in mind that figure 2a devices came from several different batches and that there were small changes in processing conditions. The J-V characteristics for several cells are plotted in **Figure IV-B-2-4** showing the best performance at just 10% polymer percentages. We are working to understand these low polymer percentages. Tapping mode AFM measurements revealed a strong correlation between blend film surface morphologies and polymer percentage. These morphologies are illustrated in **Figure IV-B-2-5**. These vastly differing morphologies may indicate that the polymer is concentrating at the surface of the anode, an undesirable phase separation that may account for the low IPCE and PCE results. Further work is in progress to establish better photovoltaic performance from these devices.



a)

b)

Figure IV-B-2-4. a) The effect of blend composition is versus PVD performance is illustrated for devices from three different batches of PTVBT:PCBM cells, and b) Current voltage behavior from cells of varied blend percentages.

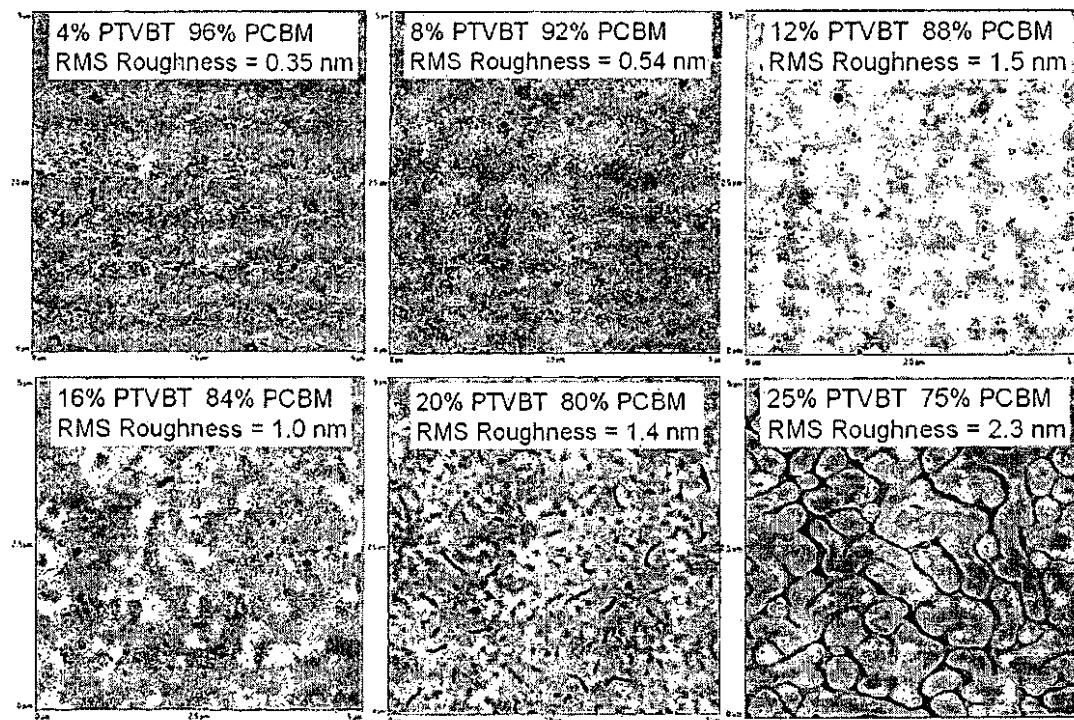


Figure IV-B-2-5. 5x5 micron AFM tapping mode images of PTVBT: PCBM blend film morphologies showing vast differences with changes in polymer percentage.

IV-B-3 Charge mobility

Charge mobility properties are important for understanding and improving conjugated polymer-based electronic devices. We have continued to employ the space-charge-limited-current(SCLC) mobility method to help us understand hole mobility in our materials. The I-V characteristics of hole-dominated devices with the configuration ITO/PEDOT-PSS/PProH:CNP(MEH)/Au, can be fit using a least squares fitting routine to the SCLC mobility equation:

$$J = \frac{9}{8} \varepsilon_r \varepsilon \mu(0) e^{\gamma \sqrt{\frac{V}{L}}} \frac{V^2}{L^3},$$

where J represents the current density, ε_r is the permittivity of the polymer, ε is vacuum permittivity, $\mu(0)$ is the zero-field mobility, g is the field dependence factor, V is applied voltage, and L is the polymer thickness. Thickness measurements are being made using an Atomic Force Microscope (AFM).

This method was employed in the investigation of p-Pt-BTD-Th and p-Pt-BTD-EDOT. The Homo level of p-Pt-BTD-Th lies at approximately 5.1 eV and the LUMO level is approximately 3.1 eV. The p-Pt-BTD-EDOT polymer has HOMO and LUMO levels at approximately 4.9 and 3.0 eV, respectively. This provides for nearly barrier-free injection of holes into the HOMO level while presenting a significant barrier for room-temperature electron injection into the LUMO level of the polymer films. These devices displayed field-dependent SCLC behavior and were fit to the following equation using the above mentioned least squares fitting routine. The room-temperature hole-mobilities of the polymer films were low for both polymers. The zero-field hole mobility (with standard error) of the p-PtBTD-Th sample was $1.4 \pm 0.3 \times 10^{-7}$ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) with a field dependence prefactor of $3.0 \pm 0.3 \times 10^{-4}$ ($\text{m}^{1/2}\text{V}^{-1/2}$). The zero-field hole mobility of the p-Pt-BTD-EDOT sample was $1.1 \pm 0.2 \times 10^{-8}$ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) with a field dependence prefactor of $3.8 \pm 0.3 \times 10^{-4}$ ($\text{m}^{1/2}\text{V}^{-1/2}$). An example of the one of the fits is shown below in **Figure IV-B-3-1**, where the polymer I-V characteristics are depicted by the black squares and the fit appears in red.

Field Dependent SCLC Mobility Fit of a 37nm p-Pt-BTD-Th Film

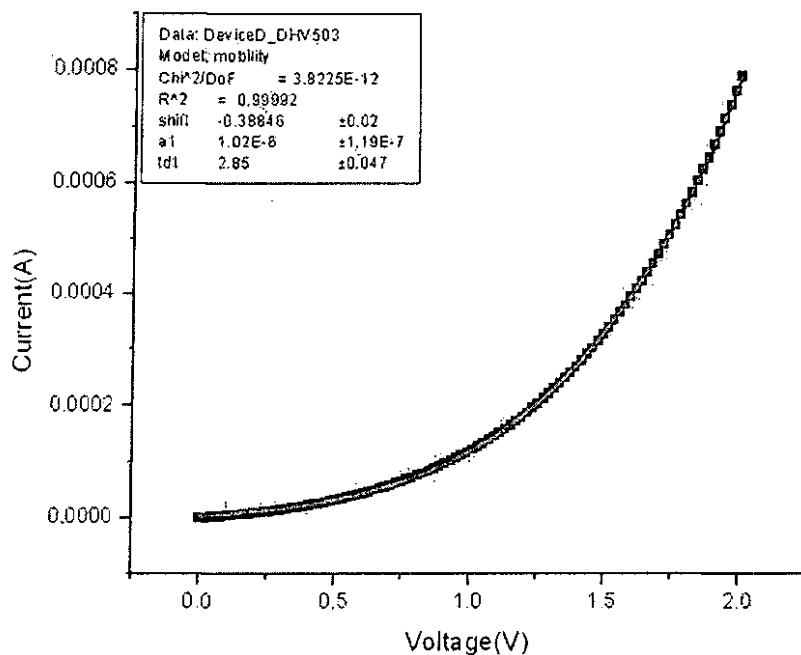


Figure IV-B-3-1. I-V curve of a 37nm p-Pt-BTD-Th thin film(black) and the field-dependent SCLC Fit(red).

IV-B-4 NIR Electrochromic Device Based on n- and p-Dopable Polymers

This work focuses on the utilization of the same electroactive polymer as both the cathode and anode switching material in an absorptive/transmissive near infrared electrochromic device. This is made possible by the use of the polymer, BisEDOT-PyrPyr-Hx₂ (shown below), which is both p-dopable and n-dopable, as the active electrochromic material. As is shown below in **Figure IV-B-4-1**, an electrochemically deposited film shows reversible p-doping and n-doping. While oxidative switching is relatively stable, the reductive switching decreases on each scan; however, the current does stabilize after 8 scans.

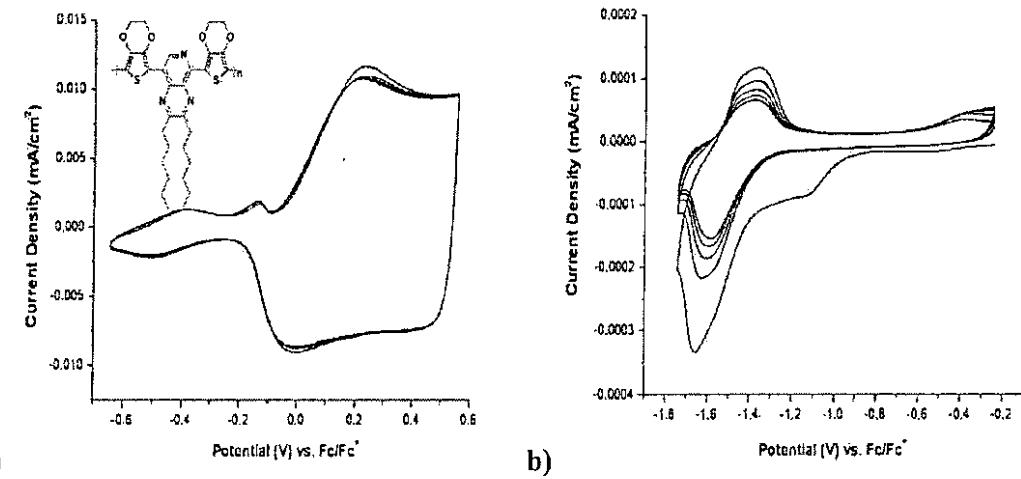


Figure IV-B-4-1. Cyclic voltammograms of BisEDOT-PyrPyr-Hx₂ in 0.2M TBAP/PC at a SWNT electrode during a) p-doping, and b) n-doping. Each scan is for 10 cycles at a scan rate of 50mV/s.

Polymer films electrochemically deposited onto ITO/glass electrodes show electrochromism, as is seen in **Figure IV-B-4-2a**. The polymer has a bandgap of 1.4 eV and is a teal-green in the neutral state and switches to a transmissive grey on oxidation. While the polymer does not show vibrant colors during electrochromic switching as would be desired for displays, it does exhibit large contrasts in the near infrared. However, as is shown in **Figure IV-B-4-2b**, the often used ITO/glass electrodes have low transmission in the near infrared of the spectrum. In fact, the transmittance drops to 50% at 1500 nm. On the other hand, the previously demonstrated SWNT electrodes have a large transmission window throughout the near infrared and even into the far IR.

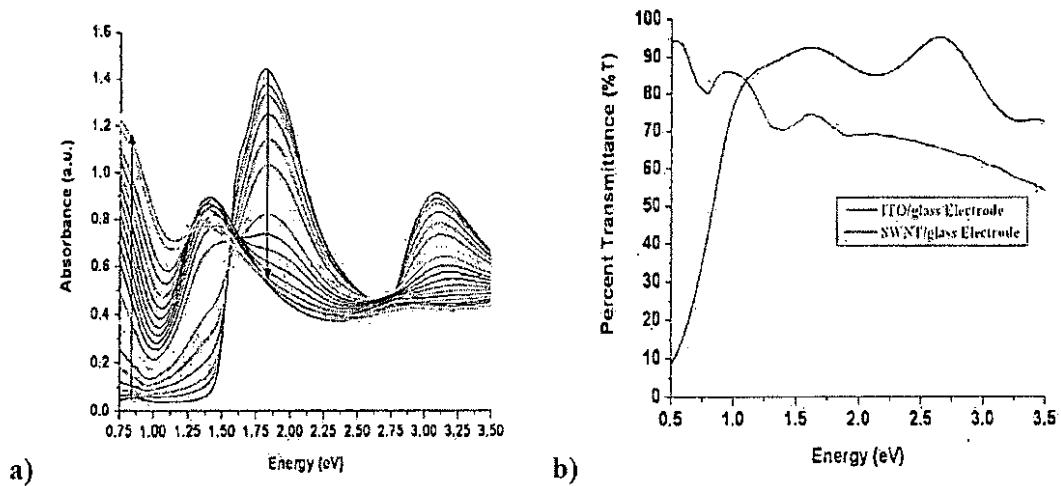


Figure IV-B-4-2. a) Spectroelectrochemistry of Poly(BisEDOT-PyrPyr-Hx₂) on ITO/glass, switched in 0.2M TBAP/PC between the potentials of -1.0 and 0.6 V vs. Fc/Fc⁺, and b) Transmission spectra of ITO/glass and SWNT/glass electrodes showing increased transmission of SWNT films in the NIR.

Films of the polymer were electrochemically polymerized onto SWNT electrodes in an argon-filled glovebox. Spectroelectrochemistry was then performed in the visible and into the NIR region of the spectrum. **Figure IV-B-4-3a** shows spectroelectrochemical switching during oxidation between the potentials of -1.0 and 0.6 V while **Figure IV-B-4-3b** shows spectroelectrochemical switching during reduction between the potentials of -1.0 and -2.0 V vs. Fc/Fc⁺. As can be seen, the spectra on p-doping on the SWNT are similar to that on the ITO/glass electrodes. On electrochemical n-doping, there is a contrast of 0.4 a.u. in the NIR. In addition, a new peak emerges centered at 2.75 eV on reduction.

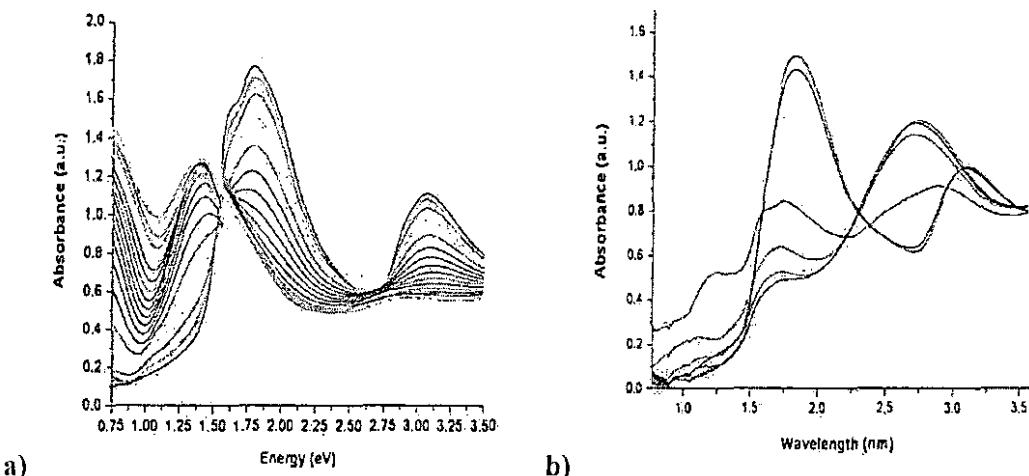


Figure IV-B-4-3. Spectroelectrochemistry of Poly(BisEDOT-PyrPyr-Hx₂) on SWNT/glass, switched in 0.2M TBAP/PC between the potentials of a)-1.0 and 0.6 V vs. Fc/Fc⁺ during p-doping, and b) -1.0 and -2.0 V during n-doping.

To capitalize on the NIR switching during both p- and n-doping, allowing the use of the same polymer in an absorptive/transmissive ECD, a device was fabricated using SWNT/glass films for both working and counter electrode, as shown schematically in **Figure IV-B-4-4a**. Additionally, **Figure IV-B-4-4b** shows the spectra when the device is at both extremes with both polymers in their neutral state at the cell potential of -0.2 V and in their respective oxidized and reduced states at -2.5 V.

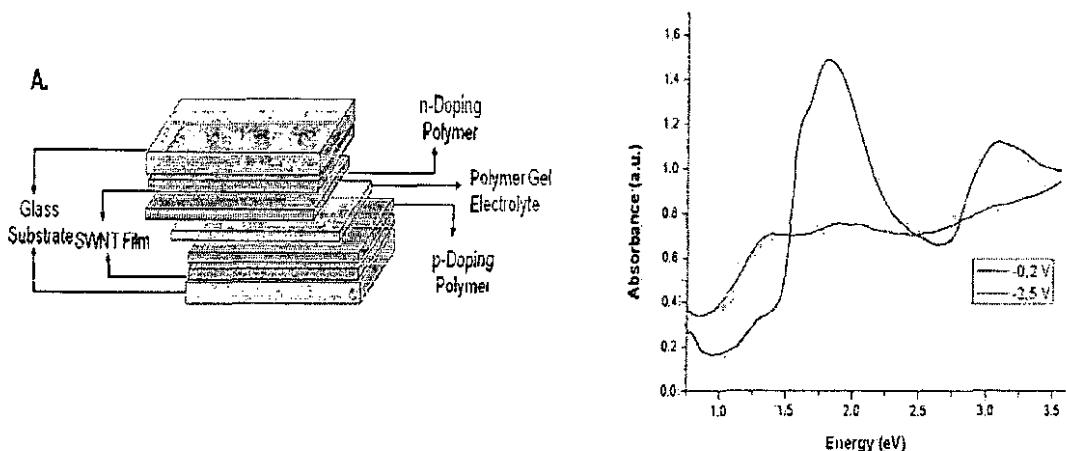


Figure IV-B-4-4. a) Schematic of SWNT absorptive/transmissive electrochromic device, and b) Spectroelectrochemistry of Poly(BisEDOT-PyrPyr-Hx₂) on SWNT/glass ECD between two extreme states.

(v) Personnel Supported with salary:

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Past Undergraduate Student:

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Other Contributing Researchers: Nicolas Berton (GS), Ken Graham (GS), Romain Stalder (GS), and Jianguo Mei (GS), David Liu (GS), Christian Nielsen (PD)

(vi) Peer Reviewed Publications that Acknowledge AFOSR:

1. Steckler, T.T., Abboud, K.A., Craps, M., Rinzler, A.G., Reynolds, J.R. *Chem. Commun.*, **46**, 4904-4906 (2007)
“Low Band Gap EDOT-Bbenzobis(thiadiazole) Hybrid Polymer Characterized on Near-IR Transmissive Single Walled Carbon Nanotube Electrodes”

2. Kim, Y.G., Christian-Pandya, H., Anathakrishnan, N., Niazimbetova, Z., Thompson, B., Galvin, M.E., Reynolds, J.R.
Sol. Energ. Mater., Sol. Cells, **92**, 307-312 (2008)
“p-OXA-X: A New Oligo Photosensitizer for Organic Solar Cells”
3. Beaujuge, P.M., Ellinger, S., Reynolds, J.R.
Adv. Mater., **20**, 2772-2776 (2008)
“Spray Processable Green to Highly Transmissive Electrochromics via Chemically Polymerizable Donor-Acceptor Heterocyclic Pentamers”
4. Nielsen, C.B., Angerhofer, A., Abboud, K.A., Reynolds, J.R.
J. Am. Chem. Soc., **130**, 9734-9745 (2008)
“Discrete Photopatternable π -Conjugated Oligomers for Electrochromic Devices”
5. Beaujuge, P., Ellinger, S., Reynolds, J.R.
Nature Materials, **7**, 795-799 (2008)
“The Donor-Acceptor Approach Allows a Black to Transmissive Switching Polymer Electrochrome”

Publications previously documented in prior reports:

1. Campos, L. M., Mozer, A. J., Gunes, S., Winder, C., Neugebauer, H., Saricifti, N. S., Thompson, B. C., Reeves, B. D., Grenier, C. R. G., Reynolds, J. R.
Sol. Energy Mat., **90**, 3531-3546 (2006).
“Photovoltaic Activity of a PolyProDOT Derivative in a Bulk Heterojunction Solar Cell”
2. Galand, E. M., Mwaura, J. K., Argun, A. A., Abboud, K. A., McCarley, T. D., Reynolds, J.
Macromolecules, **39**, 7286-7294 (2006).
“Spray Processable Hybrid 3,4-Propylenedioxythiophene: Phenylene Electrochromic Polymers”
3. Thompson, B. C., Kim, Y.-G., McCarley, T. D., Reynolds, J. R.
J. Am. Chem. Soc., **128**, 12714-12725 (2006).
“Soluble Narrow Band Gap and Blue Propylenedioxythiophene-Cyanovinylene Polymers as Multifunctional Materials for Photovoltaic and Electrochromic Applications”
4. Mauthner, G., Plank, H., List, E. J. W., Wenzl, F. P., Bouguettaya, M., Reynolds, J.R.
Phys. Rev. B, **74**, 085208-1-10 (2006).
“Photophysics of Blue Light Emitting Polymeric Mixed Ionic-Electronic Conductors: Photoluminescence and Absorption Spectroscopy”

5. Paul, G. H., Mwaura, J., Argun, A. A., Taranekar, P., Reynolds, J. R. *Macromolecules*, **39**, 7789-7792 (2006).
“Cross-linked Hyperbranched Arylamine Polymers as Hole-Transporting Materials for Polymer LEDs”
6. Galand, E., Kim, Y.-G., Mwaura, J., Jones, A. G., McCarley, T. D., Shrotriya, V., Yang, Y., Reynolds, J. R. *Macromolecules*, **39**, 9132-9142 (2006).
“Optimization of Narrow Band-Gap Propylenedioxothiophene: Cyanovinylene Copolymers for Optoelectronic Applications”
7. Walczak, R., Cowart, J. S. Jr., Reynolds, J. R. *J. Mater. Chem.*, **17**, 254-260 (2007).
“Tethered PProDOTs: Conformationally Restricted 3,4-Propylenedioxothiophene Based Electroactive Polymers”
8. Grenier, C. R., Wojciech, P., Joncheray, T. J., Müllen, K., Reynolds, J. R. *Angew. Chem. Int. Ed.*, **46**, 714-717 (2007).
“Regiosymmetric Poly(dialkylphenylenedioxothiophenes) (Poly[PheDOT(R)₂]): Electron Rich Stackable π -Conjugated Nanoribbons”
9. Berridge, R., Wright, S. P., Skabara, P. J., Dyer, A. L., Reynolds, J. R., Harrington, R.W., Clegg, W. *J. Mater. Chem.*, **17**, 225-231 (2007).
“Electrochromic Properties of a Fast Switching, Dual Colour Polythiophene Bearing Non-planar Dithiinoquinoxaline Units”
10. Dyer, A. L., Grenier, C. R. G., Reynolds, J. R. *Adv. Funct. Mater.* **17**, 1480-1486 (2007)
“A Poly(3,4-alkylenedioxothiophene) Electrochromic Variable Optical Attenuator with Near Infrared Reflectivity Tuned Independent of the Visible Region”
11. Reeves, B. D., Unur, E., Ananthakrishnan, N., Reynolds, J. R. *Macromolecules*, **40**, 5344-5352 (2007).
“Defunctionalization of Ester Substituted Electrochromic Dioxythiophene Polymers”
12. Guo, F., Ogawa, K., Kim, Y. G., Danilov, E. O., Castellano, F. N., Reynolds, J. R. Schanze, K. S. *Phys. Chem. Chem. Phys.*, **9**, 2724-2734 (2007)
“A Fulleropyrrolidine End-Capped Platinum-Acetylide Triad: The Mechanism of Photoinduced Charge Transfer in Organometallic Photovoltaic Cells”

13. Kim, Y. G., Galand, E. M., Thompson, B. C., Walker, J., Fossey, S. A., McCarley, T. D., Abboud, K. A., Reynolds, J. R.
J. Macro. Sci, Part A: **44**, 665-674 (2007)
“Isoregic Thienylene-Phenylene Polymers: The Effects of Structural Variation and Application to Photovoltaic Devices”
14. Dyer, A., Reynolds, J. R.
Handbook of Conducting Polymers, 3rd Ed., Chapter 20, pgs 1-63 (2007)
“Electrochromism of Conducting Polymers”
15. Guo, F., Kim, Y.-G., Reynolds, J. R., Schanze, K. S.
Chem. Commun., 1887-1889 (2006)
“Platinum-Acetylide Polymer Based Solar Cells: Involvement of the Triplet State for Energy Conversion”
16. Mortimer, R. J., Dyer, A. L., Reynolds, J. R.
Displays, **27**, 2-18 (2006)
“Electrochromic Organic and Polymeric Materials for Display Applications”
17. Walczak, R., Cowart, J. S., Khalil, A., Reynolds, J. R.
Chem. Commun., 1604-1606 (2006)
“Confrontational Locking for Band Gap Control in 3,4-Propylenedioxothiophene Based Electrochromic Polymers”
18. Walczak, R. M., Reynolds, J. R.
Adv. Mater., **18**, 1121-1131 (2006)
“Poly(3,4-alkylenedioxypyrrroles): The PXDOPs as Versatile yet Underutilized Electroactive and Conducting Polymers”

AFOSR Funded Publications In Press and Submitted:

N/A

Conference Presentations:

1. Material Research Society, 2007 Fall Meeting, Boston, MA, November 2007
“Variable Gap Conjugated, Organometallic and Hyperbranched Polymers in Hybrid Photovoltaic Devices” with K.S. Schanze, H., Jiang, Y.G. Kim, K.Ogawa, J. Mei, Q. Qiao, P. Taranekar
2. Materials Research Society, 2007 Fall Meeting, Boston, MA, November 2007
“Hole Mobility Studies on Thiophene-Based Conjugated Polymers and Oligomers Developed for Use in Organic Electronic Devices” with N.C. Heston, C. B. Nielsen, C.R.G. Grenier, D.B. Tanner

3. Materials Research Society, 2007 Fall Meeting, Boston, MA, November 2007
“Pt-acetylide Organometallic Polymers as Active Materials for Organic Solar Cells”
J. Mei, K. Ogawa, Y.-G. Kim, K. Schanze
4. Materials Research Society, 2008 Spring Meeting, San Francisco, CA, March 2008
“Controlled Light Absorption in Conjugated Polymers and Telechelic Oligomers for Photovoltaics and Electrochromics”
5. Materials Research Society, 2008 Spring Meeting, San Francisco, CA, March 2008
“Dual Electrochromic/Electroluminescent Displays Based on Conjugated Electroactive Polymers” with A. L. Dyer
6. Materials Research Society, 2008 Spring Meeting, San Francisco, CA, March 2008
“Discrete π -Conjugated Oligomers and their Electronic Applications” with S. Ellinger, C. Nielsen, P. Shi, R. Stalder, T.T. Steckler, P. Taranekar and N. Heston
7. Fpi-8, the 8th International Symposium on Functional n-Electron Systems, Graz, Austria, July 2008, “Spanning the Spectrum: Donor-Acceptor Concepts in Conjugated Oligomers and Polymers”
8. Fpi-8, the 8th International Symposium on Functional n-Electron Systems, Graz, Austria, July 2008, “Color Control in Pi-Conjugated Organic Polymers for Use in Electrochromic Devices” with P. Beaujuge, A. Dyer and S. Ellinger
9. Fpi-8, the 8th International Symposium on Functional n-Electron Systems, Graz, Austria, July 2008, “Multifunctional Electroactive Devices Utilizing Processable Conjugated Materials” with Aubrey Dyer, P. Beaujuge and S. Ellinger
10. Fpi-8, the 8th International Symposium on Functional n-Electron Systems, Graz, Austria, July 2008, “Donor Acceptor Based Telechelic Oligomers for NIR Emission” with S. Ellinger, P. Beaujuge and A. Dyer
11. American Chemical Society, 236th National Meeting, Philadelphia, PA, August 2008
“Conducting polymer electrochemistry: From polyacetylene batteries to supercapacitors and electrochromic displays”

Presentations previously documented in prior reports:

1. SAMPE Fall Technical Conference, Dallas, TX, Nov. 2006
“Electroactive Polymers for Carbon Composites”
2. American Chemical Society, 233rd National Meeting, Symposium on 30 years of Conducting Polymers, Chicago, IL, March 2007
“Controlled Electroactivity in Polyheterocycles”

3. American Chemical Society, 233rd National Meeting, Symposium on Conjugated Oligomers and Polymers, Chicago, IL, March 2007
“Push and Pull of Electrons in Polyheterocycles”
4. American Chemical Society, 233rd National Meeting, Chicago, IL, March 2007
“Electrochromic Conducting Polymers in Window, Display and Variable Optical Attenuator Devices” with A. L. Dyer and C. Grenier
5. American Chemical Society, 233rd National Meeting, Chicago, IL, March 2007
“Discrete Reactive Conjugated Oligomers for Electronic Devices” with C. B. Nielsen, M. M. Jacob, F. Wang and D. Rauth
6. Materials Research Society, 2007 Spring Meeting, San Francisco, CA, April 2007
“Functional and Variable Gap Conjugated Polymers in Hybrid Photovoltaic Devices” with K. S. Schanze

(vii) INTERACTIONS AND TRANSITIONS

An important element of our research effort has been to develop external interactions with government, industrial, and other academic researchers in order to more fully explore the properties of our conducting and electroactive polymers and to develop possible applications. As our research has led to the development of a broad family of new redox active electroactive polymers, they have generated significant interest from outside laboratories. We are utilizing five external interactions detailed below as routes with which to attain a higher level of materials properties characterization, along with device construction and testing. The Reynolds group has formed important liaisons with multiple companies that impact this work through collaboration or materials development for commercialization.

Present interactions and transitions:

1. **Ciba Specialty Chemicals.** Presently we have an active collaboration with Ciba Specialty Chemicals in developing electroactive and electronic materials. Ciba is now producing poly(3,4-propylenedioxyppyrroles) (100 gram scale), scaling up our cathodically coloring polymers, and is actively working with industrial partners on our electrochromic polymers.
2. **Nanoholdings/nRadiance LLC.** The University of Florida and Nanoholdings Inc. has established a new company, nRadiance Inc., to develop technology coupling transparent carbon nanotube films with our electroactive polymers and devices.
3. **Air Force Research Laboratories (AFRL).** We interact with a number of AFRL researchers at Wright-Patterson Air Force Base on a variety of levels. John Reynolds has been involved in AF program reviews and regularly visits with and discusses aspects of

electroactive polymers with the Materials Laboratory, Polymer Branch. Presently, we are collaborating on the application of conjugated polymers for photovoltaics with Michael Durstock (michael.durstock@wpafb.af.mil). Samples of new vinylene-linked polymers synthesized at UF have been studied in 2008 by the Durstock group. John Reynolds provided information on the use of conjugated polymers in solid state photovoltaic devices.

4. Crosslink. We are participating in an ARDEC supported project through Crosslink (contact Patrick Kinlen, phone 636-349-0050) on developing highly conductive and electroactive polymers for solid dielectric and supercapacitor applications. We are synthesizing functionalized 3,4-phenyldioxythiophene polymers (PPheDOT) which have the ability to stack and provide strong intermolecular π interactions as needed for high conductivity.

5. DARPA/MORPH. Donor-acceptor conjugated oligomers with acrylate functional end groups, and fully conjugated DA polymers (collaborating with the Marder group at Georgia Tech), have been developed as new two-photon absorbing coatings materials. Optical limiting behavior has been determined to be strong by the Perry group at Georgia Tech, while ambipolar charge transport in FETs has been determined by the Kippelen group.

6. Sestar LLC. The University of Florida (Karl Zawoy, 352-846-1877) has assisted in the creation of a new company, Sestar LLC, for the development of aesthetically pleasing solar cells based on colored conjugated polymers developed within our AFOSR program.

Past interactions and transitions:

1. EIC Laboratories. We are participating in an AF supported project through EIC (contact: David Rauh, 781-769-9450) on crosslinkable organic electronics. We are supplying end functionalized dioxythiophene-based oligomers with high mobilities to provide enhanced thermo-oxidative and mechanical stability. Donor-acceptor type polymers developed through our AF research are being used by EIC Laboratories in a NASA supported organic photovoltaics program.

2. Field Effect Transistors. We collaborate with Prof. Rod Devine, University of New Mexico (devine@chtm.unm.edu) on the use of conjugated polymers in organic electronics, specifically field effect transistors, with a focus towards space stability.

3. Optimized Photovoltaic Devices. We have collaborated with Prof. Yang Yang, UCLA (yangy@ucla.edu) in the optimization of photovoltaic devices using the new low gap polymers developed in our program in organic photovoltaic devices. This work has lead to a joint publication in press as noted above.

(viii) AFOSR new discoveries, inventions, or patent disclosures

Reynolds, J. R., Reeves, B., PCT/US07/61006, filed January 25, 2007; “Chemical Defunctionalization of Polymeric Alkylenedioxyheterocyclics”

Reynolds, J. R., PCT/US 2005/037893, filed 10/20/05, Issued 8/27/08; European Patent 1 812 821, France (FR1812821), Netherlands (NL1812821), Switzerland (P1812821), and United Kingdom (GB1812821); “Dual Light Emitting and Electrochromic Device”

Reynolds, J. R., Beaujuge, P. M., Ellinger, S. M., PCT/US2008/081599 filed 10/29/08; “Green Soluble Conjugated Polymers with Highly Transmissive Oxydized States”

Beaujuge, P. M. Reynolds, J. R., Ellinger, S. M., PCT/US2008/081606, filed October 29, 2008; “Black Soluble Conjugated Polymers with Highly Transmissive Oxidized States”

Beaujuge, P. M. Reynolds, J. R., Ellinger, S. M., U.S. Provisional Patent Application 61/118,316 filed November 26, 2008; “Black Soluble Conjugated Polymers with High Charge Carrier Mobilities”

(ix) Awards and Honors received by the PI (life-time received):

1. University of Florida, Research Foundation Fellowship 1999
2. V.T. and Louise Jackson Professor of Chemistry, University of Florida, College of Liberal Arts and Sciences, 2008
3. Term Professor, Colonel Allan R. and Margaret C. Crowe Professorship, University of Florida, College of Liberal Arts and Sciences, 2008